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(54) A recording sheet

(57) A recording sheet for use with pigment-based inks has a usable surface that includes a combination of a water soluble cationic substance and water soluble binder substance. The recording sheet, which may in particular be a prepared tracing paper, is calendered to a Bendtsen value of at least 200ml/min. The pigment-based ink is preferably applied to the recording sheet by an ink jet plotter or printer. The cationic substance may be a quaternary amine or a polymer and the binder may be a starch or polyvinylpyrrolidone.

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RECORDING SHEET FOR USE WITH PIGMENT-BASED INKS

The present invention relates to a recording sheet for use with printers and plotters employing pigment-based inks.

- 5 In particular, but not exclusively, the invention relates to prepared tracing paper (also known as "vellum") for use with ink jet plotters and printers. The invention is also applicable to other recording media, such as opaque papers, that are designed for use with printers and plotters
- 10 employing pigment-based inks. For example, the invention also relates to opaque papers used for graphic arts applications. Preferably, the recording media are also compatible with other types of ink and other printers.

- 15 Prepared tracing paper (as opposed to "natural" tracing paper), is manufactured from cotton-based cellulose fibre pulp that is treated with a transparentising agent, which renders the paper material translucent. The transparentising agent is an oily substance and this tends
- 20 to make the paper water-repellent. To allow inks to bond to the paper, a binder such as starch is generally applied as a surface treatment. The finished tracing paper has a smooth surface and is relatively dense and impervious, as compared to most opaque papers.

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- Prepared tracing paper has been used for many years, particularly in the USA, for the preparation of engineering master drawings to be reproduced by the diazo process. Although manual drafting has largely been superseded by the
- 30 use of CAD systems, prepared tracing paper is still used for printing the master drawings. Various types of plotter are used for printing the drawings, including pen plotters and electrostatic printers, but one of the most favoured types of plotter at present is the ink jet plotter.

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Most ink jet print heads available at present use dye-based inks. These are satisfactory for most general purpose applications such as printing text and some graphic material, but lack the density and permanence of the

pigment-based inks that have traditionally been used in the preparation of engineering master drawings. The lower density of the ink means that drawings printed using dye-based inks are not well suited to the diazo process.

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More recently, an ink-jet print head that uses pigment-based inks has become available. This print head produces denser images than the previous dye-based ink print heads and the resulting drawings are better adapted to the diazo copying process. The images are also less liable to fading than images produced using dye-based inks.

The development of the new ink jet print head has required the parallel development of new types of pigment-based ink. As the speed and definition of the print head has increased, the formulations of these new inks have been revised to provide the necessary performance.

A pigment-based ink for use with an ink jet print head typically comprises a dispersion of pigment particles, such as carbon black, suspended within an aqueous vehicle. Other ingredients, such as surfactants and stabilizers, are usually included to help maintain the dispersion, to prevent blocking of the ink jet nozzles and to promote vaporisation of the ink in the print head. However, unlike traditional pigment-based inks such as Indian ink, a binder such as shellac is not generally included as this can lead to blocking of the ink jet nozzles.

The applicants have identified a problem with existing prepared tracing paper when used with ink jet print heads employing pigment-based inks. This is that when relatively large blocks or areas (i.e. areas larger than a few mm²) of high density are printed, the print can become rather uneven. For example, the print density may be reduced towards the edges of the area and stripes or patches of varying density may be produced. This phenomenon is

sometimes referred to as "cascading". The variations in density are particularly noticeable by transmitted light and they can, therefore, be transferred to copies made by the diazo process. The effect is also noticeable to a lesser extent by reflected light and in areas of text or fine details.

The applicants have observed that the above-mentioned problem occurs when the ink droplets fall onto the paper in such a concentration that they coalesce to form a pool of liquid ink on the surface of the paper. The applicants have discovered that when this happens, the pigment particles migrate towards one another within the pool of liquid, thereby forming areas of increased density and leaving areas of reduced density.

A similar problem has been observed with colour print heads that use pigment-based black ink and dye-based coloured inks. Where an area of pigment-based ink touches an area of dye-based ink, the border between the two inks becomes scalloped with the coloured dye-based inks intruding into the black area. The applicants have discovered that this effect is caused by migration of the pigment particles away from the area of dye-based ink.

A further problem identified by the applicants is that the printed image is easily removed from the surface of the paper by abrasion. The printed documents do not, therefore, have the longevity required of them. The applicants have discovered that this is because the pigment particles tend to sit on the surface of the paper, where they are exposed to abrasive forces, rather than being drawn into the structure of the paper.

It is an object of the invention to provide a recording sheet that mitigates at least some of the above-mentioned problems.

According to a first aspect of the invention there is provided a recording sheet for use with pigment-based inks, wherein the recording sheet has a Bendtsen value of at least 200ml/min and at least a usable surface of the recording sheet includes a combination of a water soluble cationic substance and water soluble binder.

The Bendtsen value is a measure of the smoothness of the recording sheet and is determined by measuring the rate at which air passes under a circular knife edge placed on the surface of the sheet. A Bendtsen value of at least 200ml/min indicates that the recording sheet is slightly rougher than is normal for prepared tracing papers, which typically have a Bendtsen value in the range 100-200ml/min. The Bendtsen value is controlled by adjusting the pressure on the calendering rollers during the paper making process. A higher Bendtsen value is produced by decreasing the pressure on the calender rollers, which decreases the smoothness of the paper. In the present invention, therefore, the recording sheet is calendered slightly less than is normal for prepared tracing papers.

In experiments involving the application of various surface treatments to the recording sheet, the applicants have found that by treating the surface of the sheet with a water soluble cationic substance, the suspension of pigment particles can be destabilized as the ink droplets hit the surface. They have found, however, that this is not sufficient on its own to prevent migration of the pigment particles.

However, the applicants have found that if the recording sheet is calendered slightly less than normal to produce a Bendtsen value of at least 200ml/min and the surface is treated with a water soluble or water swellable binder in combination with the cationic substance, migration is largely prevented. Migration is not significantly reduced

when either of the two substances is applied without the other substance, or if the Bendtsen value of the sheet lies below the above-mentioned value. It would thus appear that the combination of treating the surface with the two substances and changing the mechanical structure of the sheet produces an unexpected synergistic effect.

Further, the applicants have found that treating the surface of the recording sheet according to the method discussed above very greatly increases the resistance of the ink to abrasion. The permanence of the printed document is thereby improved.

The cationic substance may be a quaternary amine. Alternatively, the substance may be a cationic polymer, and is preferably a low molecular weight, high cationic charge density, water soluble organic polymer. For example, the polymer may be a polymeric amine (such as a quaternary amine or easily protonated tertiary amine). An example of suitable polymer substance is a poly-quaternary amine dissolved in water.

The binder may be a chemically modified starch. For example, the starch might be oxidised or cationized by reacting it with a quaternary amine. Examples of suitable starches are oxidised potato starches and potato starch ethers. Alternatively, the binder may be a material such as polyvinylpyrrolidone (PVP).

The amount of the quaternary amine applied to the surface of the recording sheet is advantageously in the range $0.3-0.8\text{gm}^{-2}$, and more advantageously $0.5-0.7\text{gm}^{-2}$, and is preferably approximately 0.6gm^{-2} . The amount of starch applied to the surface of the recording sheet is preferably in the range $1.5-2.5\text{gm}^{-2}$ per side.

The Bendtsen value is advantageously in the range 250-

1000ml/min and preferably 300-500ml/min, and more preferably 330-470ml/min, and ideally approximately 400ml/min.

- 5 In a particularly preferred embodiment of the invention, the cationic substance is a quaternary amine, preferably a poly-quaternary amine, the binder is a chemically modified starch and the recording sheet has a Bendtsen value of approximately 400ml/min.

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The invention is particularly applicable to prepared tracing paper (Vellum). The invention may also be applicable to opaque paper and card.

- 15 According to a second aspect of the invention, there is provided a prepared tracing paper, wherein the paper has a Bendtsen value of at least 200ml/min and at least a usable surface of the paper includes a combination of a water soluble cationic substance and water soluble binder.

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According to a third aspect of the invention, there is provided an uncoated, cellulose-based paper, wherein the paper has a Bendtsen value of at least 200ml/min and at least a usable surface of the paper includes a combination
25 of a water soluble cationic substance and water soluble binder.

- According to a fourth aspect of the invention, there is provided a method of manufacturing a recording sheet for
30 use with an ink jet plotter or printer, wherein the recording sheet has a Bendtsen value of at least 200ml/min and at least a usable surface of the recording sheet is treated with a combination of a water soluble cationic substance and water soluble binder.

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The recording sheet is advantageously treated by applying an aqueous solution containing a combination of substances

to the usable surface of the sheet. Preferably, the solution is applied by drawing the semi-manufactured sheet through a bath of the solution. Alternatively, the solution may be applied to the recording sheet by spraying or coating, either during or after completion of the manufacturing process.

The desired Bendtsen value is preferably achieved by calendering the sheet. The calendering process preferably takes place during the manufacturing process, towards the dry end of that process.

According to a fifth aspect of the invention, there is provided a method of printing in which a pigment-based ink is applied to a recording sheet, wherein the recording sheet has a Bendtsen value of at least 200ml/min and at least a usable surface of the recording sheet includes a combination of a water soluble cationic substance and water soluble binder substance.

Preferably, the pigment-based ink is applied to the recording sheet by an ink jet plotter or printer.

Various embodiments of the invention will now be described by way of the following examples, in which all parts and percentages are by weight unless otherwise stated.

Example 1

An aqueous solution was applied to a sample of prepared tracing paper by a small laboratory rod coater and dried with a hot air blower. The solution contained the following substances:

Binder:	Polyvinylpyrrolidone (PVP) - 4.5%
Cation:	Quaternary amine - 5.0%
Plasticiser:	Glycerol - 4.8%

The treated paper was then calendered to a Bendtsen roughness of 100ml/min.

The performance of the paper was tested by printing a test pattern using an ink jet printer using pigment based inks. The degree of migration was assessed visually and the treated paper was found to exhibit little migration. The paper was also found to have poor abrasion resistance.

10 Example 2

A sample of prepared tracing paper was treated in the manner described above with an aqueous solution containing the following components:

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Binders: Modified starch - 3.6%
Oxidized starch - 7.2%
Cation: Quaternary amine - 5.0%

20 The treated paper was calendered to a Bendtsen roughness of 300ml/min.

The paper was found to exhibit no migration. The paper was also found to have good abrasion resistance.

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Example 3

Machine trials were performed by passing a web of semi-manufactured prepared tracing paper through a bath containing an aqueous solution having the formulation described in Example 2 above. The bath was located towards the dry end of the paper-making process, after the paper web had been drained and partially dried but before completion of the drying process. After completion of the drying process, the treated paper was calendered to Bendtsen roughness values of 300ml/min, 400ml/min and 500ml/min.

The results of the machine trials are summarised in the following tabl :

Test No.	Bendtsen value	Migration resistance	Abrasion resistance
1	300ml/min	Good	Good
2	400ml/min	Very good	Good
3	500ml/min	Very good	Good

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10 The test revealed that the best results were achieved with papers having a Bendtsen value of approximately 400ml/min. However, all the treated papers displayed a marked improvement in resistance to both migration and abrasion as compared to untreated prepared tracing papers.

CLAIMS

1. A recording sheet for use with pigment-based inks, wherein the recording sheet has a Bendtsen value of at least 200ml/min, and at least a usable surface of the recording sheet includes a combination of a water soluble cationic substance and water soluble binder.
2. A recording sheet according to claim 1, wherein the Bendtsen value of the recording sheet is in the range 250-1000ml/min, and preferably 300-500ml/min, and more preferably 330-470ml/min, and ideally approximately 400ml/min.
3. A recording sheet according to claim 1 or claim 2, wherein the cationic substance is a quaternary amine.
4. A recording sheet according to claim 1 or claim 2, wherein the cationic substance is a cationic polymer.
5. A recording sheet according to claim 4, wherein the cationic substance is an organic polymer.
6. A recording sheet according to any one of the preceding claims, wherein the binder substance is PVP or a starch.
7. A recording sheet according to claim 6, wherein the binder substance is a chemically modified starch or an oxidised starch.
8. A recording sheet according to any one of the preceding claims, wherein the amount of cationic substance applied to the surface of the recording sheet is in the range 0.3-0.8gsm, and preferably 0.5-0.7gsm, and is advantageously approximately 0.6gsm.

9. A recording sheet according to any one of the preceding claims, wherein the amount of binder substance applied to the surface of the recording sheet is in the range 1.5-2.5gsm, and preferably 1.8-2.1gsm, and is
5 advantageously approximately 2.0gsm.

10. A recording sheet according to any one of the preceding claims, in which the substances are applied to the surface of the recording sheet as an aqueous solution.
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11. A recording sheet according to any one of the preceding claims, in which the recording sheet is a prepared tracing paper.

12. A prepared tracing paper, wherein the paper has a Bendtsen value of at least 200ml/min and at least a usable surface of the paper includes a combination of a water soluble cationic substance and water soluble binder.
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13. A method of manufacturing a recording sheet for use with an ink jet plotter or printer, wherein at least a usable surface of the recording sheet is treated with a combination of a water soluble cationic substance and water soluble binder substance and the paper is calendered to a
20 Bendtsen value of at least 200ml/min.
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14. A method according to claim 13, wherein the recording sheet is treated by applying an aqueous solution of the combination of substances to the usable surface of the
30 sheet.

15. A method according to claim 14, wherein the solution is applied by drawing the semi-manufactured recording sheet through a bath of the solution.
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16. A method according to claim 15, wherein the bath is located towards the dry end of the paper manufacturing

process but upstream of the calendering rollers.

17. A method of printing, in which a pigment-based ink is applied to a recording sheet, wherein the recording sheet has a Bendtsen value of at least 200ml/min and at least a usable surface of the recording sheet includes a combination of a water soluble cationic substance and water soluble binder substance.
- 10 18. A method according to claim 17, wherein the pigment-based ink is applied to the recording sheet by an ink jet plotter or printer.



The Patent Office

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Claims searched: 1-18

Examiner: Alexander Littlejohn
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Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:
UK CI (Ed.O): B2E (EM); D1R (RBX, RDL, REX, REZ, RFA)
Int CI (Ed.6): B41M 1/36, 5/00; D21H 17/44, 17/45, 17/72, 17/74, 19/10, 19/12, 19/24, 21/14
Other: Online: WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	GB2147003A (Ricoh) see whole document, e.g. page 1 lines 33-65 and page 3 lines 16-24	1-18
X	GB1351391 (Wiggins Teape) see whole document, e.g. page 1 lines 34-42 and page 2 lines 23-48	1-18
X	EP0514633A1 (Schoeller) see whole document, e.g. claim 1	1-18
X	EP0487350A1 (Xerox) see whole document, e.g. page 4 lines 38-47 and 54,55	1-18
X	EP0423829A1 (Oji) see whole document, e.g. page 4 lines 47-50 and 54,55	1-18
X	EP0164196A1 (Mead) see whole document, e.g. pages 9,10, page 14 lines 12-29 and Example 6 on page 25	1-18
X	WPI Abstract Accession No. 89-321746/44 & JP 1241487 A (Mitsubishi) (26-09-89) see abstract	1-18
X	WPI Abstract Accession No. 88-351208/49 & JP 63264391 A (Sanyo) (01-11-88) see abstract	1-18

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.